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MODELING THE ROLE OF ORGANIC COMPOUNDS IN AEROSOL FORMATION AND CLOUD DROPLET ACTIVATION

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Modeling the Role of Organic Compounds in Aerosol Formation and Cloud Droplet Activation

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Abstract

Atmospheric aerosols are responsible for the formation of cloud droplets by acting as nuclei onto which cloud droplets are formed. This thesis investigates influences of organic compounds on the activation of cloud droplets and the growth of nanometer-sized thermodynamically stable clusters (TSCs) to sizes in which they can act as nuclei for cloud droplets. Both theoretical analyses and numerical simulations were conducted to identify properties of organic compounds that make them important regarding the considered processes.

The obtained results suggest that water-soluble organic compounds are able to influence the cloud droplet formation both by increasing the solute mass of nuclei and by reducing their surface tension. In contrast to compounds totally soluble in water, slightly-soluble compounds have clearly a smaller effect on the number of cloud droplets formed during an air updraft.

Due to a strong curvature of TSCs and nanometer-sized particles, organic compounds that might be responsible for aerosol formation at continental boundary layers could not be pinpointed in spite of an extensive search. In order to find such organic compounds, more emphasis should be put on experiments that focus on identifying atmospheric organic compounds that either 1) have a extremely low vapour pressure, or 2) react rapidly in the gas-liquid interface of TSCs or particles such that low-volatile reaction products are formed.

Keywords: cloud/climate interactions, aerosol formation, organic aerosols, heterogeneous reactions

Contents

List of publications

This thesis consists of an introductory review part, followed by five research articles.

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I Anttila, T., and Kerminen, V.-M. (2002). Influence of organic compounds on cloud droplet activation - a model investigation considering the volatility, water-solubility and surface activity of organic matter. *Journal of Geophysical Research*, doi: 10.1029/2001JD001482.

II Anttila, T., Kerminen, V.-M., and Kulmala, M. (2002). A tool for estimating the contribution of water-soluble organic compounds to the particle mass and condensational growth in the atmosphere. *Atmospheric Environment*, 36, 5897-5908.

III Anttila, T., and Kerminen, V.-M. (2003). Condensational growth of atmospheric nuclei by organic vapours. *Journal of Aerosol Science*, 34, 41-61.

IV Anttila, T., and Kerminen, V.-M. (2003). Aerosol formation via aqueous-phase chemical reactions. *Journal of Geophysical Research*, doi: 10.1029/2002JD002764.

V Anttila T, Kerminen, V.-M., Kulmala, M., Laaksonen, A., and O'Dowd, C. (2003). Modelling the formation of organic particles in the atmosphere. *Atmospheric Chemistry and Physics Discussions*, 3, 6147-6178.

1. Introduction

During the last century, gaseous and particulate emissions resulting from human activities have ended up to the Earth's atmosphere in an extraordinary pace, provoking large changes in its composition (Brasseur et al., 1999). The climatic effects of these changes are yet highly uncertain, but according to some predictions they may have far-reaching ecological and social consequences (IPCC, 2001). In order to predict reliably the fate of the climate and to assess the likely consequences, accurate knowledge on several atmospheric processes is needed. One of the most poorly known issues is the linkage between aerosol particles and clouds.

Clouds affect the radiative properties of the atmosphere by absorbing, emitting and reflecting electromagnetic radiation. The magnitudes of these effects are highly sensitive to the number and size of droplets contained by the clouds (Twomey, 1991; Baker, 1997; Hu and Stamnes, 2000). Because atmospheric aerosols are responsible for the cloud droplets by acting as nuclei onto which cloud droplets are formed, the radiative effects of clouds cannot be assessed accurately until the exact relationship between the physico-chemical properties of cloud droplets and those of atmospheric aerosols has been established.

Atmospheric aerosols contain both organic and inorganic compounds. While the inorganic aerosol component is relatively well characterized, information concerning the organic fraction is sparse at present (Jacobson et al., 2000; Turpin et al., 2000). Nevertheless, atmospheric organic compounds are suggested to influence the cloud microphysics in two important ways: by directly affecting the formation of cloud droplets and by contributing to the number of aerosols that are able to act as seeds onto which cloud droplets are formed (Novakov et al., 1997; Kerminen et al., 2000; Charlson et al., 2001; Kulmala et al., 2001). The latter includes contributions from both particles that are emitted directly to the atmosphere and particles formed through nucleation and subsequent growth to larger sizes. A considerable challenge for the

scientific community is to quantify these effects and to develop parametrizations that can be incorporated into the global climate models.

This thesis aims to improve the present understanding on the effects of atmospheric organic compounds on both cloud microphysics and growth of freshly-nucleated particles. To this end, both theoretical analyses and numerical simulations have been conducted. The primary goals are 1) to provide a new insight on the mechanisms underlying the formation and growth of cloud droplets as well as the growth of recently-formed particles, and 2) to identify which kind of organic compounds are important regarding either of these processes. To connect this work with an experimental research, the obtained results are presented so that they can be readily used in interpreting experimental data.

This thesis is organized as follows. Sections 2, 3 and 4 provide a necessary background for the conducted study, section 5 gives a brief summary of the articles contained by this thesis and section 6 presents the main conclusions of the study.

2. Organic component of atmospheric aerosols

The carbonaceous material in atmospheric aerosols can be divided into three fractions which are organic, black and carbonate carbon (Seinfeld and Pandis, 1998). Organic carbon includes hundreds of different organic compounds and, together with black carbon, forms typically the clear majority of the total aerosol carbonaceous mass in the atmosphere. Black carbon has a graphite-like structure and can be distinguished by its strong tendency to absorb visible light. Carbonate compounds present in atmospheric aerosols originate primarily from mechanical processes such as suspension of soil dust and are mainly contained by coarse particles having a diameter >1 μm. Here only the organic component is taken into account even though black carbon is also important for the ambient air quality and climate. Black carbon forms typically around 10% of the total PM2.5 (particulate matter <2.5 μm in aerodynamic diameter) mass in urban areas (Viidanoja et al., 2002 and references therein), thereby contributing to various air pollution problems. Furthermore, it may participate in various heterogenous reactions that influence atmospheric chemistry (Lary et al.,

1999) and exert a considerable heating effect on the atmosphere (Jacobson, 2001; Menon et al., 2002).

Organic compounds account for 10-70% of the total PM2.5 mass in a wide variety of atmospheric environments (Mólnar et al., 1999; Jacobson et al., 2000; Turpin et al., 2000), making them an important constituent of PM2.5 aerosol. Numerous individual organic compounds present in ambient aerosol samples have been identified (e.g. Rogge et al., 1993; Mazurek et al., 1997; Pio et al., 2001; Tsapakis et al., 2002). These compounds consist mostly of different alkanes, acids, alcohols, aldehydes, ketones, nitrates and aromatic hydrocarbons. In addition, both theoretical and experimental evidence suggest that organic sulphates and various multi-functional compounds are present in atmospheric aerosols (Saxena and Hildemann, 1996; Blando et al., 1998; Kavouras et al., 1998; Decesari et al., 2000; Fuzzi et al., 2001). However, only a minor fraction of the particulate organic matter can be identified using the present analytical methods, indicating that organic compounds present in atmospheric aerosols have extremely diverse physico-chemical properties.

2.1. Classifications of atmospheric organic compounds

In order to cope with the considerable diversity of atmospheric organic compounds, it is convenient to group, or classify, them according to various criteria. One way to classify organic compounds is to look at their molecular structure, i.e. the type and number of functional groups substituted to the molecule. Compound classes corresponding to different functional groups include organic acids (having a group –COOH), alcohols (–OH), aldehydes (-CHO), ketones (-CO) and organic nitrates (-ONO_2). Furthermore, hydrocarbons such as alkenes consist only of carbon and hydrogen atoms and thus contain no functional groups at all, whereas multi-functional compounds such as humic-like compounds have an extremely complicated molecular structure and contain several functional groups.

Typically 40-70% of the total organic mass in atmospheric aerosols is water-soluble, reflecting the varying water-solubility of individual compounds forming the organic aerosol component (Saxena and Hildemann, 1996; Shulman et al., 1996; Zappoli et al., 1999; Decesari et al., 2001; Krivácsy et al., 2001). Atmospheric organic

compounds can be divided into three main classes according to their water-solubility. Compounds dissolving entirely into water are called as water-soluble compounds, whereas slightly-soluble compounds dissolve only partially, yet at distinguishable amounts, into water. Furthermore, water-insoluble compounds exhibit only a marginal solubility into water. It should be noted that the water-solubility of a compound is related to its molecular structure. For example, those compounds having multiple functional groups tend to be polar and they therefore dissolve readily in water, whereas hydrocarbons do not exhibit significant solubility in water due to their non-polarity (Saxena and Hildemann, 1996).

The distribution of different atmospheric organic compounds between the gas and particle phases varies considerably. In this respect, three different compound classes can be distinguished. Compounds residing mostly in the particle phase are classified as “non-volatile” compounds, whereas “volatile” organic compounds (VOCs) exist entirely or to a great extent in the gas phase. In addition, “semi-volatile” compounds are able to transfer reversibly between the gas and particle phases depending on their physico-chemical properties and atmospheric conditions. The volatility of a compound is also reflected in its molecular structure. A large molecular weight and presence of multiple functional groups make a compound less volatile. Because of this, large straight-chain hydrocarbons and difunctional carboxylic acids exist primarily in the particle phase, whereas hydrocarbons having a low molecular weight stay typically in the gas phase.

Atmospheric organic compounds exhibit surface-activity to varying extent depending on their molecular structure. Compounds having a polar water-attracting group at the end of a water-repelling hydrocarbon chain are typical surface-active compounds. Such molecules tend to concentrate on the surfaces of aqueous particles, which may lead to a decrease in their surface tension (Shulman et al., 1996; Seidl, 2000). Surface-active compounds might also form coatings on the particle surface and thereby impede the transfer of different compounds between the particles and gas phase (Gill, 1983; Däumer et al., 1992; Pósfai et al., 1998; Xiong et al., 1998; Tervahattu et al., 2002). In addition, these coatings might provide a medium for chemical reactions (Ellison et al., 1999; Bertram et al., 2001; Thomas et al., 2001; Eliason et al., 2003).

2.2. Sources

The organic aerosol matter is either emitted directly into the atmosphere (primary organic aerosol formation) or formed as a result of chemical reactions taking place in the atmosphere (secondary organic aerosol formation, termed as SOA formation). The latter pathway consists of several processes, including emissions of precursor compounds, their reactions in the gas or particle phase, and transfer of reaction products between these two phases. Secondary organic aerosol could also be formed via nucleation of organic vapours, even though it is uncertain whether this takes place in the atmosphere (Gao et al., 2001; Bonn et al., 2002).

2.2.1. Primary organic aerosol formation

Globally, biomass burning and fossil fuel combustion are estimated to be resposible for most of the primary organic aerosol mass that is emitted to the atmosphere (Liousse et al., 1996). Biomass burning includes fires taking place in forests and savannas, as well as agricultural and domestic fires. Fossil fuel combustion results mainly from the burning of diesel fuels (Liousse et al., 1996; Cooke et al., 1999). These two main sources are distributed globally so that fossil fuel combustion dominates in the northern hemisphere, whereas biomass burning is concentrated on the southern hemisphere. Fossil fuel combustion has received a wide attention (Lighty et al., 2000), and comprehensive information on the particulate emissions from biomass burning are also available (Andrae and Merlet, 2001)

Other sources of primary organic aerosol include airborne degradation products of plant material and biological organisms such as bacteria and fungal spores (Jacobson et al., 2000). Furthermore, road and tire wear produce organic particulate matter in urban areas (e.g. Cabada et al., 2002). Primary organic aerosol may also be formed over the oceans resulting from the ejection of bubbles from the sea surface. These bubbles contain surface-active organic compounds which are released into the atmosphere as the bubbles burst in the air (Middlebrook et al., 1998). However, the

overall importance of this source mechanism is poorly known at the present (Jacobson et al., 2000).

2.2.2. Secondary organic aerosol (SOA) formation

The most investigated pathway for the SOA formation consists of the following steps: 1) emission of VOCs into the atmosphere, 2) their initial oxidation and subsequent gas-phase reactions and 3) uptake of one or several reaction products by particles. It has been recently suggested that secondary organic aerosol may also be formed as a result of heterogenous reactions (Blando and Turpin, 2000; Jang and Kamens, 2001; Gelencsér et al., 2002; Jang et al., 2002; Zhang and Wexler, 2002, Noziére and Riemer, 2003). However, since the experimental evidence supporting this hypothesis is yet scarce, the subsequent discussion is limited to the three-step pathway outlined above.

The following three factors determine the aerosol forming potential of any atmospheric VOC: 1) its emission rate, 2) its chemical reactivity, and 3) the tendency of its reaction products to condense into the particle phase (Seinfeld and Pandis, 1998). The emission rates of different atmospheric VOCs are quantified by field measurements, whereas the last two factors have been investigated mostly under controlled laboratory conditions. During the recent decades, the knowledge provided by these studies have been used in assessing the relative importance of various VOCs to atmospheric SOA formation.

2.2.2.1. Biogenic secondary sources

According to estimates presented by Andreae and Crutzen (1997), Griffin et al. (1999), Kanakidou et al. (2000), Chung and Seinfeld (2002), and Derwent et al. (2003), 30–270, 13–24, 61–79, 11, and 63 Tg yr^{-1}, respectively, of atmospheric particulate matter are formed globally through the oxidation of biogenic VOCs. The magnitude of these estimates are comparable to the global production of particulate sulphur which has been estimated to lie in the range 47-72 Tg S yr^{-1} (Derwent et al., 2003, and references therein). The most important biogenic VOCs forming SOA are

expected to be monoterpene compounds, even though aerosol forming potentials of many other reactive biogenic VOCs have not been fully quantified (Kesselmeier and Staudt, 1999; Fuentes et al., 2000). Monoterpenes are emitted by vegetation, mainly by coniferous trees, and they have been estimated to contribute around 10% of the global non-methane VOC emissions from natural sources (Guenther et al., 1995). Other biogenic VOCs that are emitted to the atmosphere in large amounts are isoprene, sesquiterpenes and various oxygenated hydrocarbons (Fuentes et al., 2000).

Monoterpenes such as α- and β-pinene, limonene and sabinene react rapidly in the atmosphere and produce numerous semi-volatile and volatile compounds (Kesselmeier and Staudt, 1999; Calogirou et al., 1999; Yu et al., 1999a). At daytime, the oxidation of monoterpenes is initiated by ozone or OH radical, whereas NO_3 radical dominates their initial oxidation at the night. The subsequent gas-phase reactions are extremely complex and subject to an ongoing work (e.g. Jenkin et al., 2000; Peeters et al., 2001). Several compounds resulting from the oxidation of monoterpenes that have been identified in laboratory or smog-chamber studies have also been observed in the atmosphere, including compounds such as nopinone, pinonaldehyde and pinonic, norpinonic and pinic acids (Kavouras et al., 1998, 1999; Yu et al., 1999b; Kavouras and Stephanou, 2002).

2.2.2.2. Anthropogenic secondary sources

Oxidation products of aromatic VOCs constitute the most important source for secondary organic aerosol in urban areas (Grosjean and Seinfeld, 1989; Pandis et al., 1992; Odum et al., 1997; Strader et al., 2000). The principal precursors for these reactions are toluene and various xylene and benzene compounds that are emitted from fossil fuel combustion. Their oxidation is initiated mainly by OH radical and subsequent chemistry leads to a formation of ring-retaining compounds such as phenol and to other compounds having a varying number of carbonyl and hydroxy groups (Forstner et al., 1997; Holes et al., 1997; Edney et al., 2001; Hjorth et al., 2002).

2.2.3. Primary versus secondary sources

The following question arises when assessing the contribution of different sources to atmospheric particulate matter: do primary or secondary sources dominate the organic aerosol production? Both experimental and modeling approaches have been developed to answer this question but the results are not definite (Turpin and Huntzicker, 1995; Schauer et al., 1996; Castro et al., 1999; Strader et al., 2000). This is caused both by the strong dependence of SOA formation on local conditions and by uncertainties related to these estimation methods. Nevertheless, these studies indicate that the relative importance of these two sources depend significantly on meteorological conditions, photochemical activity and local emissions.

3. Organic aerosols and clouds

Clouds are formed in the atmosphere by a rapid condensation of water vapours onto a subpopulation of aerosol particles called cloud condensation nuclei (CCN) (Pruppacher and Klett, 1980; Seinfeld and Pandis, 1998). In particular, aerosols that are able to activate grow by spontaneous condensation of water vapour into larger sizes. The rapid CCN growth results in a formation of a cloud consisting of aqueous droplets with diameters ranging from a few micrometers to several tens of micrometers. Since the size and number of cloud droplets have a significant effect on the cloud albedo and lifetime (Albrecht, 1989; Twomey, 1991; Liu and Daum, 2002), factors controlling the cloud droplet formation must be accurately known when estimating the radiative properties of the atmosphere. This highlights the importance of organic compounds as they might influence the physico-chemical properties of CCN and cloud droplet populations in several different ways.

3.1. Organic compounds and cloud droplet formation

Laboratory studies indicate that the presence of organic compounds in inorganic aerosols modifies their activation behaviour (Shulman et al., 1996; Cruz and Pandis, 1998), such that the number of resulting cloud droplets may either decrease or increase depending on the water-solubility and surface-activity of these compounds (**Paper I**; Mircea et al., 2002; Nenes et al., 2002). Water-soluble organic compounds favor the particle activation, whereas water-insoluble ones exert an opposite effect.

The influences of surface-active organic compounds are also twofold: they either enchance the cloud droplet formation by reducing the particle surface tension or suppress it by forming a film on the particle surface thereby inhibiting condensation of water vapours (Podzimek and Saad, 1975; Gill et al., 1983; Facchini et al., 1999; Feingold and Chuang, 2002). In addition, water-soluble organic vapours may condense onto particles during the cloud droplet formation, which alleviates their activation as the solute mass in aerosols is consequently increased (**Paper I**). At present, however, there is a lack of observations which would assess to what extent each of these mechanisms influence the cloud droplet formation taking place in the atmosphere.

Atmospheric organic compounds do not only modify the activation behaviour of inorganic aerosols but may also provide an additional source of cloud droplets. This has been demonstrated by laboratory experiments in which pure organic aerosols were found to activate at atmospheric supersaturations (Cruz and Pandis, 1997; Corrigan and Novakov, 1999; Hegg et al., 2001; Prenni et al., 2001; Raymond and Pandis, 2002). The same has also been observed for biomass smoke particles that contain dominantly organic matter (Novakov and Corrigan, 1996). The conducted laboratory studies are supported by field measurements which indicate that atmospheric aerosols having a significant organic component are able to act as cloud droplets (Rivera-Carpio et al., 1996; Novakov et al., 1997).

3.2. Secondary source of CCN: New particle formation

Both particles produced by direct emissions and those formed in the atmosphere contribute to the number of CCN. New particle formation, i.e. the formation of particles with diameters <10 nm and their subsequent growth up to a diameter range 50-100 nm, has been observed to take place in a wide variety of atmospheric conditions, including forests, power plant plumes, cloud outflows, polar areas and coastal sites (Mäkelä et al., 1997; Leck and Bigg, 1999; Keil and Wendisch, 2001; O'Dowd et al., 1997, 2001; Brock et al., 2002).

A first step in the atmospheric particle formation is probably the formation of thermodynamically stable clusters (TSCs) having a diameter of around one nanometer

(Kulmala et al., 2000). Under favourable conditions, TSCs grow above a detection limit and reach ultimately sizes at which they are able to act as CCN. The overall importance of this secondary CCN source is unknown at present but the observations suggest that new particle formation can take place over a synoptic scale (Nilsson et al., 2001), motivating a further study of this phenomenon. One of the major challenges in quantifying secondary CCN production is to understand mechanisms behind the observed growth of newly-formed particles in different atmospheric environments. To date, this has mainly been explained by condensation of organic vapours, sulfuric acid or iodine compounds (Leck and Bigg, 1999; Birmili et al., 2000; Kulmala et al., 2001; O'Dowd et al., 2002a, 2002b). Additionally, mechanisms involving heterogeneous reactions of organic compounds have been investigated (Zhang and Wexler 2002; **Paper IV**). The identity of organic compounds responsible for the growth of newly-formed nuclei have remained unclear but several theoretical, modeling and experimental studies elucidating their physico-chemical properties have been conducted (**Papers II-V**; Kerminen et al., 2000; Tobias et al., 2000a, 2000b; Kulmala et al., 2001; Bonn et al., 2002; Ziemann, 2002).

A critical step in the new particle formation is the uptake of vapours by growing TSCs and nanometer-size particles. More generally, this process is of crucial importance for all interactions between organic vapours and atmospheric aerosols, including the SOA formation. A theoretical basis of this study consists of different frameworks describing the gas/particle partitioning of organic compounds at a thermodynamic equilibrium. The following section contains an overview of the applied theories.

4. Gas/particle partitioning of organic compounds

Organic vapours condense on particles either by adsorbing onto their surfaces or by absorbing into a bulk thermodynamic phase. Excluding polycyclic aromatic hydrocarbons (PAHs), the absorption has been been found to be a principal gas/particle partitioning mechanism for atmospheric organic compounds (Odum et al., 1996; Goss and Schwarzenbach, 1998; Venkataraman et al., 1999; Dachs and Eisenreich, 2000; Cousins and Mackay, 2001). Even if particles were solid, a bulk phase is expected to form once a few monolayers of organic compound molecules have adsorbed to the particle surfaces (Pankow, 1994a). After this, absorption

dominates the uptake. It can thus be concluded that adsorption does not play a major role in the overall gas/particle partitioning of organic compounds and therefore only the absorption is considered here.

4.1. Absorptive phase partitioning

Two different absorption mechanisms are applied in this thesis. First of them, the so-called Henry's law, describes absorption of water-soluble compounds by an aqueous phase (Saxena and Hildemann, 1996; Seinfeld and Pandis, 1998). According to the Henry's law, the equilibrium partial pressure of a compound *i*, $P_{eq,i}$ (atm), over a flat surface can be expressed as follows:

$$P_{eq,i} = \frac{c_i}{H_i \gamma_i}, \quad (1)$$

where c_i (M) is the concentration of the compound *i* in the solution, H_i (M atm^{-1}) is the Henry's law constant and γ_i is the activity coefficient of the compound *i* in the solution. It should be noted that here c_i refers to the concentration of the compound *i* in a non-dissociated form. Dissociation increases the uptake of a compound beyond that predicted by equation (1). This can be treated by replacing H_i with a so-called effective Henry's law constant (Seinfeld and Pandis, 1998). However, if the compound *i* undergoes other chemical reactions in the aqueous phase, more elaborate frameworks are required to determine its uptake accurately (Hanson et al., 1994). The effect of the particle curvature to the gas/particle partioning can be accounted for by including the Kelvin term into equation (1) (e.g. **Paper III**).

A gas/particle partitioning theory developed by Pankow, Bowman and co-workers (Pankow, 1994a, 1994b, Odum et al., 1996: Bowman et al., 1997) describes the absorption of organic compounds by a liquid-like organic phase. This theory predicts that in a thermodynamic equilibrium, the following equation holds for the concentration of an organic compound *i*, $C_{eq,i}$ (μg m^{-3}), over a flat surface:

$$C_{eq,i} = \frac{m_i}{K_{om,i}\, m_{om}}. \quad (2)$$

Here m_i (g) is the mass of the compound i in the, m_{om} (g) is the total organic mass of the absorbing phase, and $K_{om,i}$ (m^3 μg^{-1}) is the gas/particle partitioning parameter which can be written as follows:

$$K_{om,i} = \frac{RT}{10^6 MW_{om} P_{sat,i} \gamma_{i,om}}, \quad (3)$$

where R (8.206×10^{-5} m^3 atm mol^{-1} K^{-1}) is the ideal gas constant, T (K) is the temperature, MW_{om} (g mol^{-1}) is the average molecular weight of the absorbing material, and $\gamma_{i,om}$ is the activity coefficient of the compound i in the organic phase. The effect of the particle curvature to a compound uptake can be treated similarly as in the case of the Henry's law.

It is worth noting that both of the above-presented theories are based on a fundamental thermodynamic equation called as the Raoult's law (Denbigh, 1981; Pankow, 1994a; Saxena and Hildemann, 1996). Furthermore, the parameters H_i and $K_{om,i}$ play analogous roles in these two theories, since they both describe to what extent a compound is absorbed by a thermodynamic phase. For convenience, a unit of partial pressure is used in the Henry's law, whereas the latter theory is formulated using a unit of mass concentration. If required, these two units can be converted to each other by applying the ideal gas law.

4.2. Thermodynamic models

Atmospheric aerosols contain typically concentrated mixtures of compounds having highly diverse physico-chemical properties. Such compounds are likely to exhibit strong deviations from an ideal behaviour, which should be taken into account when determining their gas/particle partitioning. At present there are several models capable of treating these non-idealities.

Group contribution methods such as UNIFAC can be applied to calculating the activity coefficients of organic compounds present in the particle absorbing phase

(Jang et al., 1997; Saxena and Hildemann, 1997; Ansari and Pandis, 2000, Pankow et al., 2001, Seinfeld et al., 2001, Chandramouli et al., 2003). These techniques describe a solution containing organic compounds as a sum of the functional groups present in these compounds. Mutual interactions of dissolved compounds can be therefore treated using a relatively small number of parameters (e.g. Poling et al., 2000). In a case of compounds containing two or more strong polar groups, however, UNIFAC usually fails to predict the activity coefficients accurately, since it does not take into account for the mutual interactions between these polar groups (Saxena and Hildemann, 1997).

More comprehensive thermodynamic approaches that treat solutions containing both organic and inorganic compounds have also been developed (Clegg et al., 2001; Ming and Russell, 2002; Pun et al., 2002; Griffin et al., 2003). Depending on the approach, mutual interactions of organic and inorganic compounds are either neglected or are treated explicitly by conducting thermodynamic calculations that utilize the available experimental data. Excluding the frameworks developed by Pun et al. (2002) and Griffin et al. (2003), these approaches have been applied only to some model systems for which all the required thermodynamic data are available. Overall, their applicability to atmospheric modeling is limited at present due to a lack of information concerning the physico-chemical properties of atmospheric organic compounds.

4.3. Gas/particle partitioning of organic compounds under atmospheric conditions

The Henry's law have traditionally been applied only to compounds having a high or infinite water-solubility, whereas the theory developed by Pankow, Bowman and co-workers was used originally to interpret results from smog-chamber experiments that studied SOA formation resulting from the oxidation of various VOCs (Odum et al., 1996; Bowman et al., 1997). However, besides being limited to the investigation of pure organic aerosols, these experiments were conducted in dry chambers. This arises the question that is especially important regarding the atmospheric applications of these two theories: how does the presence of water and inorganic salts in aerosols affect the absorption of organic compounds? Given that atmospheric aerosols contain

often an aqueous phase, it remains also unclear which is the appropriate gas/particle partitioning mechanism for water-soluble and slightly-soluble organic compounds.

Recent smog-chamber experiments have addressed the question presented above by investigating aerosol formation resulting from the ozone-initiated oxidation of α-pinene (Cocker et al., 2001). The findings of these experiments that are relevant to the present discussion are summarized in Table 1.

Table 1. Some results of the smog-chamber experiments carried out by Cocker et al. (2001). Here RH refers to relative humidity at the chamber during the experiment. Seed aerosols, if used, are injected into the chamber to provide a medium into which reaction products are able to condense initially.

RH	Composition of seed aerosol	Absorbing phase(s) present in the aerosols and their composition
dry	none	pure organic phase
elevated	none	water-containing organic phase
dry	ammonium bisulfate, ammonium sulfate or natrium chloride	pure organic phase
elevated	aqueous ammonium bisulfate, ammonium sulfate or natrium chloride	possibly multiple phases

The observed gas/particle partitioning of reaction products under dry conditions is consistent with their absorptive uptake by the particle organic phase, even when inorganic seed aerosols have been present. This conclusion agrees also with the results obtained from previous smog-chamber experiments (Odum et al., 1996; Bowman et al., 1997; Liang et al., 1997; Pankow et al., 2001).

The experiments conducted under humid conditions are more difficult to interpret. When only organic compounds and water have been present in the aerosols, it has been concluded that these compounds formed an absorbing phase that behaves non-

ideally to some extent. Accordingly, the simple absorptive framework developed by Pankow, Bowman and co-workers is valid under these conditions. This model predicts, however, that the uptake of organic compounds would increase when aqueous seed aerosols containing inorganic salts are introduced to the chamber, in contrast to what has been observed. To address this discrepancy, a more detailed thermodynamic model was applied. Even though it could not produce the measured aerosol formation accurately, its predictions were closer to the measurements than those of the simpler model. Furthermore, the model predicted that the aerosols contained eventually two separate liquid-like phases. One of the phases consisted mostly of inorganic compounds, whereas organic compounds were dominant in the other phase. This finding indicates that the presence of water in internally mixed organic/inorganic aerosols may give rise to highly complex phase interactions. In particular, it implies that atmospheric organic compounds may be absorbed by both organic and aqueous phases co-existing in aerosols.

4.4. Phase model for gas/particle partitioning of organic compounds

This thesis contains an approach to modeling the absorption of organic compounds by aqueous aerosols and cloud droplets containing both organic and inorganic compounds. As seen from Figure 1, particles and cloud droplets are assumed to have two phases. First of them is an aqueous solution containing dissolved inorganic and organic compounds and the second one is a liquid-like organic phase. Organic compounds are treated by lumping them into three classes according to their solubility in water. Water-soluble and water-insoluble compounds are assumed to be absorbed solely by the aqueous and organic phase, respectively. Slightly-soluble compounds are absorbed by the organic phase, from which they dissolve into the aqueous phase according to their water-solubility. Here the water-solubility of slightly-soluble compounds is kept as a free parameter. Furthermore, the Henry's Law is used in determining the equilibrium gas-particle partitioning of water-soluble compounds, whereas equation (2) is used for the two other compound classes. These calculations are carried out by keeping the gas/particle partitioning parameters H_i and $K_{om,i}$ constant within each of the three compound classes.

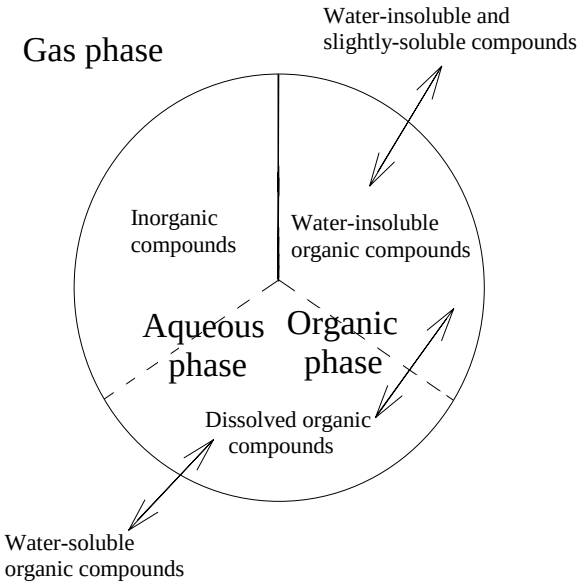

Figure 1. A schematic diagram illustrating how semi-volatile organic compounds partition between the gas phase and different phases present in an aerosol particle and/or cloud droplet.

The approach described above is particularly useful for atmospheric modeling, since it allows for the consideration of organic compounds having highly heterogeneous properties. For example, it has been applied for investigating the effects of organic compounds on the cloud droplet formation taking place in the atmosphere (**Paper I**). The drawback in the developed approach is that it neglects deviations from an ideal behaviour, in particular mutual interactions between the organic and aqueous phases. However, when appropriate thermodynamic data become available, they can be incorporated to this framework to treat non-ideal solutions.

5. Review of the papers

This thesis consists of modeling and theoretical studies on the effects of organic compounds on the cloud droplet and new particle formation taking place in the atmosphere. **Paper I** focuses on cloud droplet formation, whereas the other papers deal with various mechanisms underlying the growth of very small atmospheric particles. **Papers II** and **III** consider the physico-chemical properties of organic vapours that make them important to the particle condensational growth, whereas **Paper IV** investigates whether aqueous-phase chemical reactions might be

responsible for new particle formation. Finally, **Paper V** accounts for both organic vapours and gaseous sulfuric acid in modeling the formation of organic particles from thermodynamically stable clusters having a diameter of around one nanometer.

Paper I is a model study on the influence of organic compounds on cloud droplet activation. In order to treat the heterogeneous properties of atmospheric organic compounds, four different compound classes were taken into account: water-soluble and water-insoluble compounds that stay in particles and cloud droplets, and slightly-soluble and water-soluble compounds that condense reversibly from the gas phase to particles and cloud droplets. The obtained results suggest that water-soluble organic compounds are able to influence the cloud droplet formation via two mechanisms: 1) by increasing the solute mass of particles or cloud droplets, and 2) by reducing their surface tension. Compared to compounds that are totally soluble in water, it was found that the majority of the slightly-soluble organic compounds has much smaller impact on cloud droplet formation.

Paper II investigates the relative roles of semi-volatile and "non-volatile" organic vapours in the condensational growth of newly-formed particles. It was found that the Kelvin effect has two important consequences in a case of such small particles. First, it limits considerably the uptake of organic vapours, and therefore only "non-volatile" compounds having a very low vapours pressure are able to grow nanometer-size particles significantly. Second, due to the strong sensitivity of the Kelvin term to the particle size at the diameter range <30 nm, an initially semi-volatile compound may ultimately exceed the considerable "barrier" imposed by the Kelvin effect and start to contribute the particle growth like any "nonvolatile" vapours. Furthermore, a saturation vapours pressure required for any organic compound to behave like a "non-volatile" vapours was derived. The most important factors in this respect were the particle diameter, its chemical composition and physico-chemical properties of the condensing compound such as its gas-phase concentration, water-solubility and molecular weight. The derived requirements were also validated against simulations performed on a numerical model.

Paper III is a theoretical study on factors that make any water-soluble organic vapours important to either the SOA formation or to particle condensational growth in

the atmosphere. This study provides quantitative criteria that can be applied in investigating whether a given atmospheric organic compound is able to influence either of the considered processes significantly. Important factors regarding these two processes were shown to be the saturation ratio of a condensing compound, its hygroscopic properties and tendency to dissociate in the aqueous phase, as well as the particle size, pH, and surface tension. Furthermore, the derived requirements were compared with the physico-chemical properties of several difunctional carboxylic acids identified in the atmosphere. The conducted comparison suggests that while many of the considered compounds are expected to contribute to the total particulate mass, they are unlikely to explain the condensational growth of nanometer-size particles formed in the atmosphere.

Paper IV considers the growth of recently-formed particles via chemical reactions taking place in the particle aqueous phase. These reactions were assumed to be initiated by a semi-volatile organic compound and to produce compounds that stay in the particle aqueous phase. It was demonstrated, however, that such reactions are likely to be suppressed by the strong Kelvin effect. This led to the conclusion that other heterogeneous growth mechanisms, e.g. chemical reactions taking place in the gas-liquid interface are more viable to induce a rapid particle growth. In addition, the results from a recent laboratory study investigating SOA formation in the particle phase were analyzed.

Paper V applies a recently developed theory, the so-called nano-Köhler theory, to explain how organic particles are formed from freshly-nucleated TSCs. The nano-Köhler theory implicates that after reaching a certain threshold size, TSCs are ”activated”, i.e. they start growing rapidly due to spontaneous condensation of a water-soluble organic vapours. By conducting numerical simulations, it was demonstrated that condensation of gaseous sulfuric acid plays a key role in growing freshly-nucleated clusters to sizes in which they are able to activate. These simulations along with theoretical considerations revealed also that meteorological processes such as dilution and adiabatic cooling of the air masses may influence the cluster activation considerably. Self-coagulation was found to grow these clusters effectively into larger sizes only during very intense nucleation bursts. Furthermore, the results were shown to be consistent with the seasonal characteristics of aerosol

formation events that has been observed during continuous measurements carried out at a remote site in a central part of Finland.

6. Conclusions

Effects of atmospheric organic compounds on cloud droplet formation and growth of newly-formed particles have been investigated. Both theoretical analyses and numerical simulations were conducted in order to elucidate which kind of organic compounds are able to influence the considered processes. Quantitative criteria that can be applied to identify such compounds were also derived.

The results of this thesis provide a qualitative picture on the condensational growth of freshly-nucleated particles due to organic vapours. After nucleated particles have reached a certain threshold size, they become “activated” with respect to low-volatile organic vapours. This results in a rapid particle growth due to spontaneous condensation of these vapours and, under favourable conditions, leads to an apparent particle formation. The conducted model simulations revealed that condensation of gaseous sulfuric acid is typically needed to grow newly-formed particles to sizes in which they are able to activate, implying that a shortage of gaseous sulfuric acid may limit the formation of particles having detectable sizes.

Organic compounds that might be responsible for growth of freshly-nucleated particles at continental boundary layers could not be pinpointed in spite of a extensive search. This is due to an intense Kelvin effect which inhibits effectively condensation of all organic vapours into such small particles, excluding those having a very low saturation vapours pressure. In order to find plausible candidate compounds for the growth of recently-formed particles, more emphasis should be put on experiments that focus on identifying atmospheric organic compounds that either 1) have an extremely low vapour pressure, or 2) react rapidly in the gas-liquid interface such that “non-volatile” compounds are formed.

The influences of atmospheric organic compounds on the cloud droplet formation were also considered by applying a phase partitioning model for organic compounds that was developed in this thesis. The obtained results suggest that water-soluble

organic compounds are able to influence the cloud droplet formation by increasing the solute mass of particles or cloud droplets and by reducing their surface tension. In contrast to compounds entirely soluble in water, slightly-soluble compounds have clearly a smaller effect on the number of cloud droplets formed during an updraft.

The major uncertainties in this thesis arise from an incomplete knowledge concerning the identity and physico-chemical properties of atmospheric organic compounds. In addition, these compounds may also interact with other atmospheric compounds in complex ways that are poorly understood at present. This necessitated a simplified treatment of organic compounds, especially what it comes to their thermodynamics, in this thesis. In order to reduce the related uncertainties, more field measurements and laboratory experiments investigating the physico-chemical properties of atmospheric organic compounds are needed.

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